

Reactivity of Halogenotetrakis(phosphite)cobalt(II) Complexes with Nitric Oxide. Characterization and Properties of New Pentacoordinate Mononitrosyl Cobalt Complexes

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The reaction of NO with $[CoXL_4]^+$ ($X = Cl, Br, I$; $L =$ phosphites) cations has been studied and new pentacoordinated mono- and tetraordinated dinitrosyl cobalt complexes, $\{MNO\}^8$ and $\{M(NO)_2\}^{10}$, obtained in mild conditions. Trigonal-bipyramidal structures with linear MNO have been deduced from infrared and pmr spectra for the mononitrosyl compounds described. The reactivity with phosphine, CO, halogen, and isocyanide of the nitrosyl complexes reported is also presented as well as the investigations carried out to ascertain the species operating the reduction to cobalt(I) in the formation of dinitrosyl complexes.

Introduction

The synthesis, structure and reactivity of nitrosyl cobalt complexes have been studied extensively [1–3]. Tetra- and pentacoordinate nitrosyl-phosphine mixed ligand derivatives of this metal have been obtained by several methods including: a) the reaction of mono or bidentate phosphines on $[CoX(NO_2)_2]$ ($X =$ halogen) compounds [4], b) phosphine substitution reaction by NOPF₆ on $[Co(CO)(NO)L_2]^+$ ($L =$ trialkylphosphine) complexes [5], c) NO addition to tetrahedral $[CoX_2L_2]$ and $[CoP(CH_3)_3]_4$ derivatives [6, 7]. Except for the work of Chatt [6] and that of Caulton [8] on the reductive nitrosylation on cobalt(II) compounds, very few data are known on the reactivity of nitric oxide on phosphine cobalt(II) complexes [2b].

We have previously reported [9] on the reactivity of CO with halogenotetrakis(diethylphenylphosphite) cobalt(II) complexes with special reference to the stoichiometry and nature of carbonyl intermediates. To better understand the reactivity of $[CoXL_4]^+$ derivatives with reducing ligands and to compare these results with those obtained with CO, the

present study of the reactivity of NO on the same cobalt(II) compounds has been undertaken. This allowed us to synthesize new nitrosyl-phosphine derivatives by simply using gaseous NO under mild conditions. Furthermore, the presence of better π -acceptor phosphines should make these nitrosyl-products different from those already reported as far as their chemical and catalytic properties are concerned.

Experimental

Materials and Apparatus

All solvents used were purified by standard methods and distilled under nitrogen just prior to use. Anhydrous $CoCl_2$ was prepared by heating the commercial hexahydrate under vacuum at 60–80 °C for 12–16 hours, while anhydrous CoI_2 was obtained by refluxing the dihydrate with 2,2-dimethoxypropane. Dimethoxyphenylphosphine and diethoxyphenylphosphine were prepared by the method of Rabinowitz and Pellon [10]. Trimethyl- and triethylphosphite were 'Baker' chemical products and were purified by distillation under nitrogen. Nitric oxide (Baker) was purified by passing it through a –80 °C trap. All other reagents were used as received.

Infrared spectra of KBr pellets and dichloromethane solutions were recorded on a Perkin-Elmer 457 or 508 spectrophotometer. Proton NMR spectra were obtained using Bruker HFX-10 and/or Varian EM 390 instruments with tetramethylsilane as an internal standard.

The Evans method [11] was used to test the diamagnetism in solution. Conductivities of $10^{-3} M$ solutions of complexes in nitromethane at 25 °C were measured with an Haloisis bridge.

Measurements of gas uptake were carried out in a glass vacuum system, using standard techniques [8]. At constant pressure the volume of NO taken up was measured by a gas-buret apparatus using the procedure previously described [9].

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$[\text{CoXL}_4]\text{BPh}_4$ ($X = \text{Cl, Br, I; L} = \text{PhP(OMe)}_2$ and PhP(OEt)_2 ; $X = \text{I; L} = \text{P(OMe)}_3$ and P(OEt)_3)

These complexes were obtained following the method used for the synthesis of the diethoxyphenylphosphine derivative [12]. To a solution of anhydrous CoX_2 (10 mmol) in 80 ml of methanol or ethanol, the appropriate phosphite (50 mmol) was added. The addition of NaBPh_4 (10 mmol) caused the precipitation of a green product which was recrystallized from dichloromethane-ethanol (yield $\geq 70\%$). The elemental analyses, I.R. and UV spectra, conductivity and magnetism of the complexes were in agreement with the proposed formula.

$[\text{CoIL}_3(\text{NO})]\text{BPh}_4$ ($L = \text{P(OMe)}_3, \text{P(OEt)}_3$)

Freshly prepared $[\text{CoIL}_4]\text{BPh}_4$ (25 mmol) in anhydrous acetone (80 ml) previously flushed with NO, was vigorously stirred at room temperature under a NO atmosphere 3 hours for the P(OEt)_3 derivative and 16 minutes for the P(OMe)_3 compound.

The brown solution was reduced in volume, using a rotary evaporator, to give an oil which was then stirred vigorously with ethanol at -5°C . The solid thus obtained was recrystallized at room temperature from dichloromethane-ethanol (yield $\geq 80\%$).

$[\text{CoCl}[\text{P(OEt)}_3]_3(\text{NO})]\text{BPh}_4$

To a solution of anhydrous CoCl_2 (10 mmol) in ethanol (80 ml) P(OEt)_3 (40 mmol) was added. Bubbling NO through the solution for 20–30 minutes caused a change of color from blue to green. The addition of NaBPh_4 after 2–3 hr afforded a green solid which was recrystallized from dichloromethane-ethanol (yield $\geq 60\%$).

$[\text{CoL}_2(\text{NO})_2]\text{BPh}_4$ [$L = \text{P(OMe)}_3, \text{P(OEt)}_3, \text{PhP(OMe)}_2, \text{PhP(OEt)}_2$]

Nitric oxide was bubbled for one day through a vigorously stirred solution of $[\text{CoIL}_4]\text{BPh}_4$ [$L = \text{P(OMe)}_3, \text{P(OEt)}_3, \text{PhP(OMe)}_2, \text{PhP(OEt)}_2$] (10 mmol) in anhydrous acetone (80 ml). The brown solution was brought to dryness and ethanol (30–50 ml) was added. After 2–3 hours of vigorous stirring at -5°C , a red-brown crystalline solid separated out. This was filtered, washed with ethanol and diethyl-ether, then dried *in vacuo* and recrystallized from dichloromethane-ethanol (yield $\geq 40\%$).

$[\text{CoI}[\text{PhP(OEt)}_2]_2(\text{NO})_2]$

This compound formed simultaneously with the $[\text{Co}[\text{PhP(OEt)}_2]_2(\text{NO})_2]\text{BPh}_4$ complex when NO was passed through a solution of $[\text{CoI}[\text{PhP(OEt)}_2]_4]\text{BPh}_4$ for one day. After the $[\text{Co}[\text{PhP(OEt)}_2]_2(\text{NO})_2]\text{BPh}_4$ complex separated out, the title complex was crystallized by cooling the ethanol solution to -30°C for 2–3 days. The red-brown crystals were washed with ethanol and dried *in vacuo* (yield $\geq 35\%$). To

avoid decomposition the product was stored in a sealed tube under nitrogen and kept at -30°C .

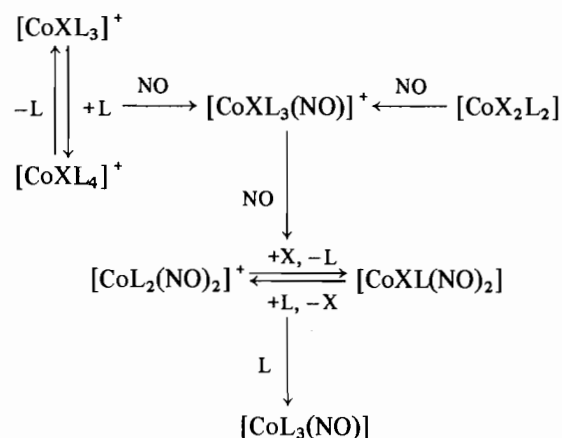
$[\text{Co}[\text{PhP(OEt)}_2]_3(\text{NO})]$

Diethoxyphenylphosphine (5 mmol) was added to a solution of $[\text{Co}[\text{PhP(OEt)}_2]_2(\text{NO})_2]\text{BPh}_4$ (1 mmol) in 20 ml of acetone or dichloromethane. After one day the solution was evaporated to dryness and 10–20 ml of ethanol was added under stirring. By cooling the mixture to -30°C , red crystals separated out which were washed with ethanol, dried *in vacuo* and stored in a sealed tube under nitrogen (yield 20%).

The $[\text{CoL}_2(\text{NO})_2]\text{BPh}_4$ complexes are stable in the solid state and in solutions of organic polar solvents. The $[\text{CoXL}_3(\text{NO})]\text{BPh}_4$, $[\text{CoIL}(\text{NO})_2]$ and $[\text{CoL}_3(\text{NO})]$ compounds are air sensitive and their solutions must be prepared just prior to use.

Results and Discussion

The reaction of cobalt(II) halides with phosphites affords complexes of the type $[\text{CoXL}_4]^+$ [$X = \text{Cl, Br, I}$ if $L = \text{PhP(OEt)}_2$ or PhP(OMe)_2 ; $X = \text{I}$ if $L = \text{P(OEt)}_3$ or P(OMe)_3] and $[\text{CoX}_2\text{L}_2]$ [$X = \text{Cl, Br}$ and $L = \text{P(OEt)}_3, \text{P(OMe)}_3$] [12, 13]. At room temperature both complexes $[\text{CoXL}_4]^+$ and $[\text{CoX}_2\text{L}_2]$ take up NO at 1 atm, with the formation of five-coordinate mononitrosyl cations of the type $[\text{CoXL}_3(\text{NO})]^+$, which further react with NO to produce dinitrosyl complexes of the type $[\text{CoL}_2(\text{NO})_2]^+$ and $[\text{CoXL}(\text{NO})_2]$, as shown in the following scheme:



Scheme 1

The progress of the reaction can be conveniently followed by recording the IR spectra of the reaction mixture, since well separated bands in the coordinated NO stretching region are observed. When the

TABLE I. Physical Constants and Analytical Data for the Complexes.

Compound	Color	Mp ^a °C	Λ_M^b cm ² ohm ⁻¹ mol ⁻¹	%C		%H		%N		%X	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
{Co[P(OCH ₃) ₃] ₃ (NO)}BPh ₄	Brown	87	47.8	43.68	43.03	5.22	5.13	1.54	1.59	13.99	13.80
{Co[P(OC ₂ H ₅) ₃] ₃ (NO)}BPh ₄	Brown	91	49.4	48.81	49.36	6.34	6.64	1.35	1.32	12.28	12.19
{CoCl[P(OEt) ₃] ₃ (NO)}BPh ₄	Green	89	48.8	53.54	53.31	6.96	6.73	1.49	1.62	3.76	4.02
{Co[P(OCH ₃) ₃] ₂ (NO) ₂ }BPh ₄	Orange	91	54.6	52.50	52.49	5.58	5.59	4.08	4.06	—	—
{Co[P(OC ₂ H ₅) ₃] ₂ (NO) ₂ }BPh ₄	Red-Orange	55	56.0	56.12	55.80	6.54	6.20	3.64	3.56	—	—
{Co[PPH(OCH ₃) ₂] ₂ (NO) ₂ }BPh ₄	Red-Brown	78	55.9	61.71	62.41	5.44	5.30	3.60	3.69	—	—
{Co[PPH(OC ₂ H ₅) ₂] ₂ (NO) ₂ }BPh ₄	Red-Brown	84	54.3	63.32	63.30	6.04	5.79	3.36	3.24	—	—
{Co[PPH(OC ₂ H ₅) ₂](NO) ₂ }	Red-Brown	93	—	27.05	27.12	3.40	3.62	6.31	6.19	28.58	28.45
{Co[PPH(OC ₂ H ₅) ₂] ₃ (NO)}	Orange	120	—	52.71	52.33	6.64	6.39	2.05	2.01	—	—

^aMelting points were determined in capillaries and are uncorrected. ^bMolar conductances (Λ_M) were determined in 10⁻³M nitromethane solutions at 25 °C.

[CoXL₄]⁺ complexes are allowed to react with NO, a strong absorption appears at first, in the 1780–1802 cm⁻¹ region, which can be attributed to the [CoXL₃(NO)]⁺ derivatives. The reaction rate increases in the order PhP(OMe)₂ \approx PhP(OEt)₂ > P(OMe)₃ > P(OEt)₃ and the addition of free phosphine ligand to the reaction mixture decreases the corresponding absorption rate of NO. Taking into account the existence of the equilibrium [12] [CoXL₄]⁺ \rightleftharpoons [CoXL₃]⁺ + L it is reasonable to assume that the formation of mononitrosyl complexes is due to the following addition reaction: [CoXL₃]⁺ + NO \rightarrow [CoXL₃(NO)]⁺. Furthermore also the mononitrosyl derivatives react with NO with a rate depending on the nature of phosphine ligand as reported above. It follows that only the pure compound [CoX(P(OEt)₃)₃(NO)]⁺ or [CoX(P(OMe)₃)₃(NO)]⁺ can be isolated by stopping the reaction after 180 or 16 minutes, respectively. But when the phosphine is PhP(OEt)₂ or PhP(OMe)₂ even by quenching the reaction after a short time (2 minutes) we always obtained an impure product containing both the mono- and dinitrosyl species, as can be deduced from the IR spectrum.

Further reaction of NO on the mononitrosyl species gives an IR spectrum in which the 1780–1802 cm⁻¹ band is replaced by four absorptions in the regions 1858–1876, 1806–1817, 1837–1848, and 1777–1790 cm⁻¹ due to the [CoL₂(NO)₂]⁺ and [CoXL(NO)₂] products. Moreover by adding free ligand to the reaction mixture the [CoL₃(NO)] complexes are formed, as can be deduced from the IR spectra (ν_{NO} 1673–1685 cm⁻¹).

As was pointed out above and reported in Scheme 1, the [CoX₂L₂] complexes also react with NO to give the pentacoordinated mononitrosyl compounds, [CoXL₃(NO)]⁺. Such a behaviour was unexpected and can be attributed to the peculiar properties of the phosphites because by using PR₃ phosphines as ligand the reaction of [CoX₂L₂] with NO gives only the mononitrosyl [CoX₂L₂(NO)] complexes [6].

While all the tetracoordinated complexes with PhP(OEt)₂ can be easily crystallized, it has not been possible to isolate the [CoXL(NO)₂] and [CoL₃(NO)] derivatives with the PhP(OMe)₂, P(OMe)₃ and P(OEt)₃ ligands, since intractable oils were obtained. However, the [Co(P(OEt)₃)₃(NO)] complex has been recently obtained [15] as pale-orange crystals by electrochemical reduction of the [CoI(P(OEt)₃)₃(NO)]⁺ cation. The [CoI(PhP(OEt)₂)(NO)₂] and [Co(PhP(OEt)₂)₂(NO)₂]⁺ complexes can also be quantitatively obtained by passing NO through a 2.5 \times 10⁻² M dichloromethane solution of [CoI(PhP(OEt)₂)₂(CO)₂] at room temperature. Under the same conditions the [Co(PhP(OEt)₂)₄(CO)]⁺ compound gives the [Co(PhP(OEt)₂)₂(NO)₂]⁺ cation.

The mixed ligand phosphine-nitrosyl cobalt complexes reported here are diamagnetic in the solid state and in solutions of polar organic solvents such as

acetone, dichloromethane, nitromethane and ethanol. The elemental analyses (Table I), IR and NMR spectra and conductivity data have been used to confirm formulas of all the new complexes. The $[\text{CoIL}(\text{NO})_2]$ and $[\text{CoL}_3(\text{NO})]$ are non-conducting, whereas $[\text{CoIL}_3(\text{NO})]\text{BPh}_4$ and $[\text{CoL}_2(\text{NO})_2]\text{BPh}_4$ are 1:1 electrolytes [17]. The previously reported nitrosyl complexes of the type $[\text{CoL}_2(\text{NO})_2]^+$ and $[\text{CoXL}(\text{NO})_2]$ (L = triphenylphosphine or bis(diphenylphosphine) ethane, ethylenediamine, phenanthroline, nitriles and olefins) [4, 8, 1f] have been obtained by reaction of the ligand with the halodinitrosylcobalt complexes $[\text{Co}(\text{NO})_2\text{X}]_n$. Only in one case has nitric oxide been used as a reducing and nitrosylating agent, to obtain the $[\text{Co}(\text{PPh}_3)_2(\text{NO})_2]^+$ complex by reaction of $[\text{CoCl}_2(\text{PPh}_3)_2]$ with NO in basic ethanol [8]. Mononitrosyl $[\text{CoL}_3(\text{NO})]$ complexes with phosphines such as PPh_3 and PhPMe_2 are also known but they have been obtained by reducing the $[\text{CoL}_2(\text{NO})_2]^+$ or $[\text{Co}(\text{NO})_2\text{Cl}]_n$ derivatives with sodium amalgam [4].

Furthermore we tried to determine the nature of the species operating in the redox process. The results obtained can be summarized as follows: a) the two dinitrosyl complexes are formed in quantitative yield; b) phosphine oxide is present in the final reaction mixture; c) the mol ratio between the absorbed NO and the $[\text{CoXL}_4]^+$ complex falls in the range 3.9–4.4. It is known that free phosphine, which can act as a reducing agent [16], is directly oxidized by NO [7] with quantitative formation of nitrous oxide and phosphine oxide. Therefore, in our case, it is difficult to decide which is the reducing species. However, since $[\text{CoL}_3(\text{NO})]$ is obtained quantitatively by reaction of phosphine with the $[\text{CoXL}_3(\text{NO})]^+$ complexes (see below) the important reducing capabilities of the phosphine ligand should not be underestimated.

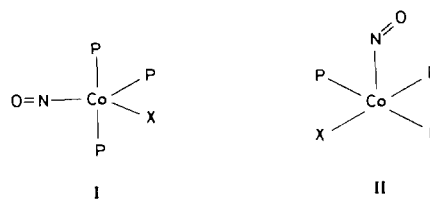
A comparison of the reactivity of $[\text{CoXL}_4]^+$ with NO or CO [9] indicates that in both cases the first step is not a substitution reaction but an addition reaction to form the $[\text{CoXL}_3(\text{NO})]^+$ or $[\text{CoXL}_3(\text{CO})]^+$ derivatives. While the mononitrosyl compounds can be isolated, the monocarbonyls have been obtained in solution and never isolated in pure form. Clearly, the extra electron of NO stabilizes the diamagnetic mononitrosyl more than does CO the paramagnetic monocarbonyl. In both cases the most complicated step is reduction to dinitrosyl or dicarbonyl complexes of the type $[\text{CoIL}(\text{NO})_2]$, $[\text{CoL}_2(\text{NO})_2]^+$, $[\text{CoXL}_2(\text{CO})_2]$ and $[\text{CoL}_3(\text{CO})_2]^+$. However while CO has been proved to reduce cobalt(II) to cobalt(I) complexes, no clear evidence has been obtained on the ability of NO to operate in the same way. It has not been possible to isolate a mononitrosyl $[\text{CoL}_3(\text{NO})]^+$ complex corresponding to the $[\text{CoL}_4(\text{CO})]^+$ compound, but $[\text{CoL}_3(\text{NO})]$ can be obtained by further reduction of the dinitrosyl derivatives with phosphine.

IR and NMR Spectra

The IR spectra of $[\text{CoX}(\text{P}(\text{OEt})_3)_3(\text{NO})]^+$ (X = Cl, I) complexes show a strong band at 1780 cm^{-1} (X = Cl) or at 1792 cm^{-1} (X = I) in the solid state and at 1781 cm^{-1} or at 1791 cm^{-1} , respectively, in CH_2Cl_2 solution. Since these observed values and their relative corrected ones fall above 1620 cm^{-1} , one can suppose that the CoNO group is linear, according to the empirical rules proposed by Haymore and Ibers [18].

The NMR spectrum of $[\text{CoCl}(\text{P}(\text{OEt})_3)_3(\text{NO})]^+$ cation shows in the phosphine methyl region two triplets at 8.69τ ($J = 7\text{ Hz}$) and at 8.74τ ($J = 7\text{ Hz}$; 2:1 ratio) (Table II). A quintet at 6.08τ (7 Hz) and a multiplet at 5.82τ ($J = 3.6\text{ Hz}$) with a ratio 1:2 due to the methylene protons, indicate that two equivalent phosphines are *trans* and that they are different from the third. At ambient temperature the analogous iodo derivative exhibits a triplet at 8.71τ ($J = 7\text{ Hz}$) due to the methyl protons and a multiplet at 6.28τ due to the methylene protons. On cooling the solution to -40°C the methyl protons resonance splits into two triplets at 8.69τ and 8.64τ (ratio 2:1) and the methylene protons signal splits into a quintet and a multiplet at 5.75τ and at 5.55τ . These facts seem to indicate that the $[\text{CoI}(\text{P}(\text{OEt})_3)_3(\text{NO})]^+$ complex has a non-rigid structure at room temperature.

A trigonal bipyramidal geometry with a linear M–N–O angle (I) and a tetragonal pyramidal geometry with strongly bent coordinated NO (II), have been proposed for five-coordinate $\{\text{MNO}\}^8$ complexes [3].



The $[\text{CoCl}_2(\text{PR})_3(\text{NO})]$ complexes show indeed two stretching frequencies in the NO region with a difference of $60\text{--}100\text{ cm}^{-1}$ and with an intensity ratio dependent on the nature of the phosphine and on the temperature [19, 6b]. These data have been explained in terms of the coexistence of the two isomers I and II. On the contrary, in our case the IR and NMR data suggest that the pentacoordinate $[\text{CoX}(\text{P}(\text{OEt})_3)_3(\text{NO})]^+$ (X = Cl or I) complexes present a type I structure.

The existence of only one conformer can be attributed to the presence of three good π -acceptor phosphine ligands; this agrees with the theoretical studies of Hoffmann *et al.* [3b] suggesting that the presence of good π -acceptor ligands favors structure I with the NO group in the equatorial position. This is confirmed by the spectral data of the $[\text{CoI}(\text{P}(\text{OME})_3)_3-$

TABLE II. Selected IR and PMR Data for some Nitrosyl Complexes.

Compound	ν_{NO} in solution ^a and (solid) ^b , cm^{-1}	Chemical Shift (τ) ^d	
		CH ₂	CH ₃
[Co][P(OCH ₃) ₃] ₃ (NO)]BPh ₄	1802s (1788)s	6.21d(12Hz) ^e	6.37q
[Co][P(OC ₂ H ₅) ₃] ₃ (NO)]BPh ₄	1791s (1792)s	8.64t(7Hz) ^e	8.71t
[CoCl{P(OC ₂ H ₅) ₃] ₃ (NO)]BPh ₄	1781s (1780)s	5.55m(3.6Hz)	5.75qi(7Hz) ^e
[Co][P(OCH ₃) ₃] ₂ (NO) ₂]BPh ₄	1876s (1871)s	6.06	6.28m
[Co][P(OC ₂ H ₅) ₃] ₂ (NO) ₂]BPh ₄	1869s (1858)s	6.06	6.08qi(7Hz)
[Co][PPh(OCH ₃) ₂] ₂ (NO) ₂]BPh ₄	1864s (1850)s	6.66	6.48
[Co][PPh(OC ₂ H ₅) ₂] ₂ (NO) ₂]BPh ₄	1858s (1859)s	6.21	8.74t
[Co][PPh(OC ₂ H ₅) ₂] ₂ (NO) ₂]	1837s (1838)s	5.94qi(7Hz)	8.76t
[Co][PPh(OC ₂ H ₅) ₂] ₃ (NO)]	1673s (1675)s	6.25qi(7Hz)	8.62t(7Hz)
[Co][P(OC ₂ H ₅) ₃] ₃ (NO)]	1680s ^c (1679)s	6.03qi(7Hz)	8.83t(7Hz)

^a In CH₂Cl₂ solution. ^b In KBr pellets. ^c Ref. 15. ^d In CDCl₃. ^e In (CD₃)₂CO at -40 °C.

(NO)]BPh₄ complex which shows only a strong absorption at 1802 cm⁻¹. Furthermore in the NMR spectrum the quartet at 6.37 τ which appears in the methyl region at room temperature is split into a triplet (6.10 τ ; J = 6 Hz) and a doublet (6.27 τ , J = 12 Hz; intensity ratio 2:1) at -40 °C, indicating that two apical phosphines are present as shown in structure I.

In the solid state and in CH₂Cl₂ solution two IR bands at 1858–1876 cm⁻¹ and at 1806–1817 cm⁻¹ (Table II) are observed in the NO stretching region for the dinitrosyl complexes of the type [CoL₂(NO)₂]BPh₄ (L = PhP(OMe)₂, PhP(OEt)₂, P(OMe)₃ and P(OEt)₃) indicating that the MNO groups are linear.

Besides a doublet due to the methyl protons, centered at 6.48 τ and 6.66 τ (J = 12 Hz), respectively, the NMR spectra of the P(OMe)₃ and PhP(OMe)₂ derivatives show a weak single peak resonance at the same frequencies (Fig. 1). The intensity ratio between the doublet and the singlet is solvent and temperature dependent in the range -50 °C, +100 °C. In the methyl region the NMR spectra of the P(OEt)₃ and PhP(OEt)₂ derivatives show a triplet at 8.74 τ and at 8.76 τ (J = 7 Hz), whereas in the methylene region the same complexes exhibit a complicated pattern centered at 6.06 τ and at 6.21 τ respectively, which can be seen as a quintet superimposed on a multiplet (Fig. 2). Also in this case the intensity ratio between

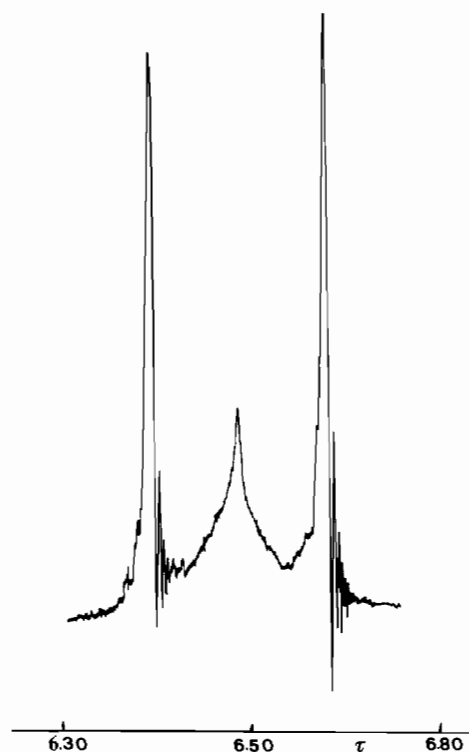


Fig. 1. PMR spectra of the [Co(P(OMe)₃)₂(NO)₂]BPh₄ complex in (CD₃)₂CO.

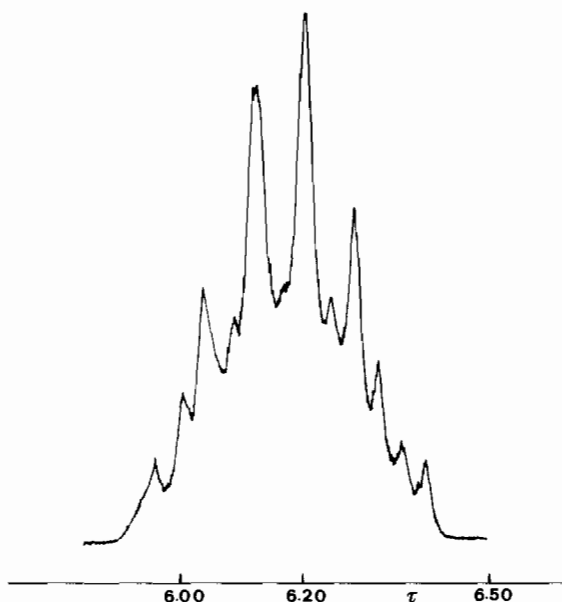
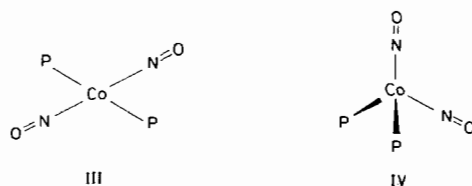


Fig. 2. PMR spectra in the methylene region of the [Co(PhP(OEt)₂)₂(NO)₂]BPh₄ complex in (CD₃)₂CO.

the quintet and the multiplet is solvent and temperature dependent. Furthermore, by decoupling the methylene protons signal from the methyl protons a pattern similar to that shown in Fig. 1 was obtained.

The geometry of these tetracoordinate compounds can be discussed in terms of two limiting structures, *i.e.* a tetrahedral or a square planar arrangement around the metal atom. For the [Co(PPh₃)₂(NO)₂]⁺ and [Co(dpe)(NO)₂]⁺ (dpe = bis(diphenylphosphine)ethane), {M(NO)₂}¹⁰ complexes, a pseudo-tetrahedral structure has been reported [20, 21]. In our case, the NMR spectra seem to a first approximation, to suggest the existence in solution of both isomers III and IV.



Taking into account that in cobalt(I) complexes containing P(OMe)₃ ligands the J_{PH} app (6 Hz) is half the J_{PH} (12 Hz) [9b], as we also found for [CoI(P(OMe)₃)₃(NO)]⁺ cation, the doublet centered at 6.48 τ and at 6.66 τ for P(OMe)₃ and PhP(OMe)₂ derivatives respectively, can be attributed to the tetrahedral geometry IV, whereas the signal present at the same frequency may be tentatively assigned to the central line of a triplet due to a III-type geometry. Similarly the quintet at 6.06 τ and 6.21 τ for the P(OEt)₃ and PhP(OEt)₂ tetracoordinate derivatives respectively (attributable to a tetrahedral geometry) is super-

imposed on a multiplet which may result from a square planar structure. No further contribution on the existence of a square planar geometry may be achieved from the IR spectrum because these complexes show quite broad absorptions in the 1858–1876 cm^{-1} and 1806–1817 cm^{-1} regions, where a III-type structure should present its own absorption when MNO is linear. Preliminary data of the X-ray crystal structure of $[\text{Co}(\text{P}(\text{OMe})_3)_2(\text{NO})_2]\text{BPh}_4$ indicate the existence of a pseudo-tetrahedral structure [22].

Reactivity

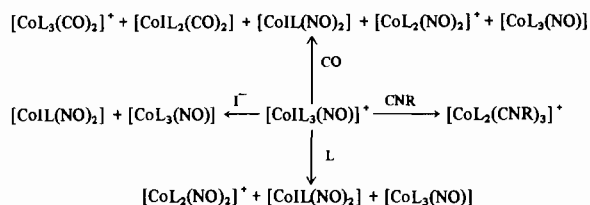
The reactivity with phosphine, CO, halogen and isocyanide of the penta- and tetracoordinate nitrosyl complexes here reported has been tested.

The pentacoordinate mononitrosyl $[\text{CoIL}_3(\text{NO})]^+$ ($\text{L} = \text{P}(\text{OEt})_3$ or $\text{P}(\text{OMe})_3$) compounds react with Γ^- affording the $[\text{CoIL}(\text{NO})_2]$ and $[\text{CoL}_3(\text{NO})]$ complexes. The change of the $\Gamma^-/\text{complex}$ ratio in the 1–10 range does not influence the nature of the products. Quite surprisingly we have not been able to observe the equilibrium $[\text{CoIL}_3(\text{NO})]^+ + \Gamma^- \rightleftharpoons [\text{CoL}_2(\text{NO})] + \text{L}$ as found for tetracoordinate nitrosyl derivatives [4]. The IR spectra of CH_2Cl_2 solutions do not show any absorption attributable to $[\text{CoL}_2(\text{NO})]$ derivatives.

When phosphine ligand is added to a iodotris(phosphite)nitrosylcobalt solution the $[\text{CoIL}(\text{NO})_2]$, $[\text{CoL}_2(\text{NO})_2]^+$ and $[\text{CoL}_3(\text{NO})]$ complexes are obtained. By operating with a $\text{L}/[\text{CoIL}_3(\text{NO})]^+$ ratio greater than ten the mononitrosyl $[\text{CoL}_3(\text{NO})]$ only is formed in quantitative yield. This suggests that the phosphine and not the NO is the reducing agent.

The $[\text{CoI}(\text{P}(\text{OEt})_3)_3\text{NO}]^+$ pentacoordinate mononitrosyl complex reacts at room temperature with CO (1 atm) to give the corresponding $[\text{CoIL}_2(\text{CO})_2]$, $[\text{CoL}_3(\text{CO})_2]^+$, $[\text{CoIL}(\text{NO})_2]$, $[\text{CoL}_2(\text{NO})_2]^+$ and $[\text{CoL}_3(\text{NO})]$ derivatives. On following the progress of the reaction by recording the IR spectrum of the solution, four bands in the CO stretching region at 2040, 1998, 1975 and 1935 cm^{-1} are observed. The first two bands can be attributed to the $[\text{Co}(\text{P}(\text{OEt})_3)_3(\text{CO})_2]^+$ cation whereas the other two bands to the $[\text{CoI}(\text{P}(\text{OEt})_3)_2(\text{CO})_2]$ complex. The same carbonyl complexes can be prepared by reaction of $[\text{CoXL}_4]^+$ with CO [13]. Furthermore, the characteristic absorptions of the $[\text{CoIL}(\text{NO})_2]$, $[\text{CoL}_2(\text{NO})_2]^+$ and $[\text{CoL}_3(\text{NO})]$ nitrosyl complexes are also present. The yields of the nitrosyl products are always very high (95% compared to the amount of NO in the starting complex) even when the reaction mixture is allowed to stand under CO for 3–4 days. These results seem to indicate that the affinity of NO in these cobalt derivatives is higher than that of the CO and therefore the substitution of nitric oxide by CO does not take place.

Isocyanides react with the $[\text{CoIL}_3(\text{NO})]^+$ cation to give complexes of the type $[\text{Co}(\text{CNR})_3\text{L}_2]^+$ [9b]; the same complexes are also obtained starting from the tetracoordinate $[\text{CoL}_2(\text{NO})_2]^+$ cations. These results are summarized in the following scheme:



The dinitrosyl $[\text{CoL}_2(\text{NO})_2]^+$ [$\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, $\text{PhP}(\text{OMe})_2$, $\text{PhP}(\text{OEt})_2$] complexes react with X^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) according to the well known equilibrium $[\text{CoL}_2(\text{NO})_2]^+ + \text{X}^- \rightleftharpoons [\text{CoXL}(\text{NO})_2] + \text{L}$ and with phosphites to give $[\text{CoL}_3(\text{NO})]$ and/or $[\text{CoL}_4]$ compounds depending on the concentration of ligand used. It must be pointed out that no reaction has been observed by treating at room temperature these tetracoordinate dinitrosyl complexes with CO.

The oxidation of the mononitrosyl $[\text{CoL}_3(\text{NO})]$ [$\text{L} = \text{PhP}(\text{OEt})_2$, $\text{P}(\text{OEt})_3$] complexes in acetone or CH_2Cl_2 with AgClO_4 gives the $[\text{CoL}_2(\text{NO})_2]^+$ cation whereas both $[\text{CoIL}(\text{NO})_2]$ and $[\text{CoL}_2(\text{NO})_2]^+$ complexes are obtained when I_2 is used. However, these reactions are not quantitative and their stoichiometry needs further investigation.

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